SYNTHESIS OF ALGINATE STABILIZED GOLD NANOPARTICLES BY γ-IRRADIATION WITH CONTROLLABLE SIZE USING DIFFERENT Au^{3+} CONCENTRATION AND SEED PARTICLES ENLARGEMENT

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Abstract: Gold nanoparticles with pre-selected size in the range of 5-40 nm were synthesized by γ-irradiation of Au^{3+} solution containing natural polysaccharide alginate as a stabilizer. The gold nanoparticles with controllable size were prepared by two approaches: i) varying the concentration of Au^{3+} from 0.25 to 1 mM and alginate from 0.25 to 1 % (w/v) and ii) enlargement of seed particles with double size from 20 to 40 nm at $[Au^{3+}]/[Au^{0}]=6$. The obtained gold nanoparticles were characterized by UV-vis spectroscopy and transmission electron microscopy. The results indicated that γ-irradiation method is suitable for production of gold nanoparticles with controllable size and high purity.

Keywords: *Gold nanoparticles, Sodium alginate, Seed enlargement, γ-irradiation.*

I. INTRODUCTION

Synthesis and characterization of gold and other noble metals nanoparticles have gained considerable attention due to their diversity applications in different nanoscale science and engineering, such as in catalysis [4, 26], antioxidation [9], pharmacy [1, 2, 3, 14], sensor [5, 27],.. . A number of techniques have been reported for the synthesis of gold nanoparticles (Au-NPs), such as chemical [9, 15, 23, 27, 28, 29], photochemical [25], sonochemical [6, 19] and radiolytic [11, 12, 17] reduction. Among these techniques, the radiation-induced synthesis is one of the most promising strategies because it contains several advantages as compared to conventional chemical and photochemical methods [12, 17].

Change in size causes the gold nanoparticles to have different properties that are suitable for utilizations in biomedicine [24] and cosmetics (www.utilisegold.com). Therefore, the preparation of gold nanoparticles with controllable size is an attractive field of research. It is the fact that reproducible synthesis of the stable particles with desired size is a difficult task. A few systematic approaches were used to synthesize particles with pre-chosen size by varying the concentration of Au^{3+} and stabilizer [10, 16] or by seed-mediated growth [11, 12, 25]. Because Au-NPs can be used in biological application such as DNA sensors [18], drug delivery [21, 30], cancer diagnostic and therapy [7, 8, 22], preparation of a biocompatible and nontoxic system containing Au-NPs is a challenge task. Although methods for the preparation of Au-NPs using chemicals as reducing and/or stabilizing agents such as citrate, borohydride, or other organic compounds are being widely applied, they may associate with environmental toxicity or biological hazards. Recently, some works have introduced a green method using natural polymers, such as chitosan [15], D-glucose and soluble starch [23] as reducing and stabilizing agents for synthesizing Au-NPs. In this particular way, Pal et al. (2005) prepared Au-NPs by UV photoactivation in the presence of sodium alginate as stabilizer. Sodium alginate extracted from seaweeds, a natural polysaccharide with a large available quantity in nature composed of three types of block polymers namely polyguluronate (poly-G), polymannuronate (poly-M) and copolymer of poly-G and -M in random sequences [13]. Sodium alginate is biocompatible and widely used for food and drink, pharmaceutical and bioengineering industries. For the biological perspective reason, in this work we used sodium alginate as a stabilizer for radiolytic synthesis of Au-NPs with controllable size via varying the content ratio of Au^{3+}/alginate and seed particles enlargement.

II. EXPERIMENTAL

1. Materials:

Hydrogen tetrachloroaurate (III) trihydrate ($HAuCl_4 \cdot 3H_2O$) and pure water were obtained from Merck, Germany. Sodium alginate (M_n = 4.35 × 10^5 g/mol) was a product of Hayashi Pure Chemical Industries Ltd., Japan.

2. Preparation and characterization of gold nanoparticles:

In a typical experiment, 1 ml of 10 mM $HAuCl_4$ was added to 5 ml of 2 % (w/v) aqueous alginate solution, then the mixture was filled with water to the final volume of 20 ml for obtaining solution of 0.5 mM Au^{3+}/0.5 % alginate . After thorough stirring, the mixture was sealed and irradiated at dose of 8 kGy on a Co-60 source at VINAGAMMA Center, Ho Chi Minh City with dose rate of 1.3 kGy/h at ambient temperature. The obtained Au-NPs solution was used as seeds for further particles enlargement. One part of the 1 mM Au-NPs solution was mixed with two, four, six and eight parts of a solution containing 1 mM Au^{3+}/0.5 % alginate. The overall gold concentration ($[Au^0] + [Au^{3+}]$) in this mixture was again 1 mM, but the Au^{3+} concentration was from two to eight times larger than that of Au-NPs.

The UV-vis spectra of the obtained Au-NPs solutions which were diluted by water to 0.1 mM calculated as Au^{3+} concentration were recorded using UV-vis spectrophotometer model UV-2401PC, Shimadzu, Japan. The size of Au-NPs was characterized by transmission electron microscope (TEM) model JEM 1010, JEOL, Japan operating at 80 kV.

III. RESULTS AND DISCUSSION

1. Effect of Au^{3+} concentration

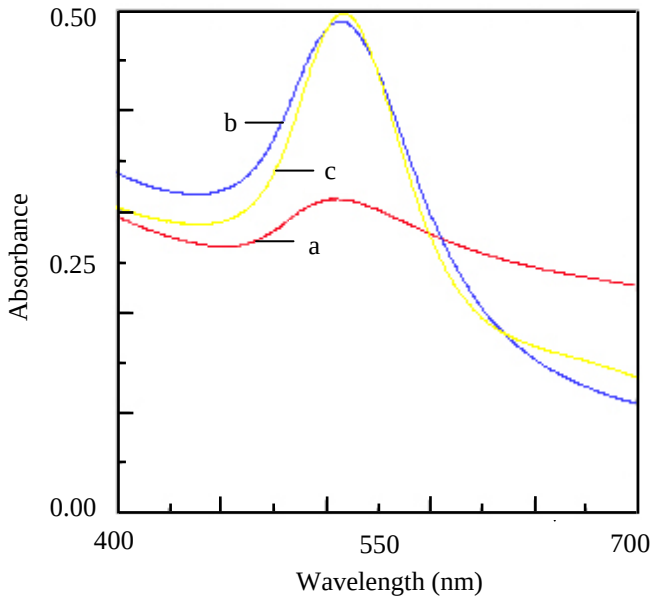

Figure 1. UV-vis spectra of Au-NPs stabilized by 0.5 % (w/v) alginate with Au^{3+} concentrations: 0.25 mM (a); 0.5 mM (b) and 1 mM (c).

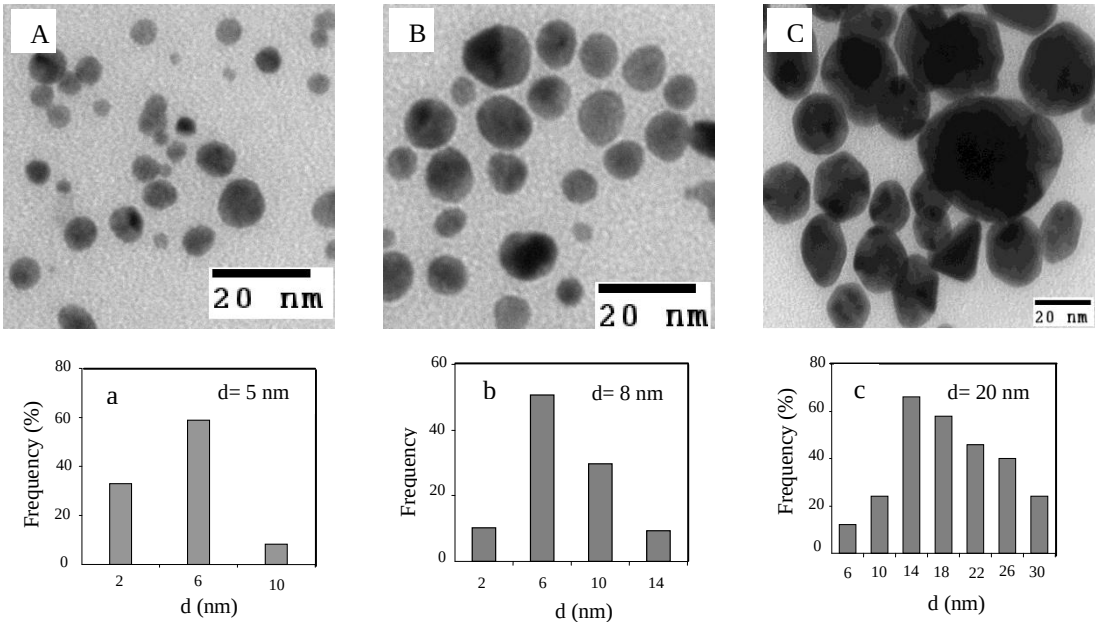

Figure 2. TEM images and size distribution histograms of Au-NPs stabilized by 0.5 % (w/v) alginate with Au^{3+} concentrations: 0.25 mM (A, a); 0.5 mM (B, b) and 1 mM (C, c).

In this first experiment, Au-NPs were prepared from samples containing 0.5 % (w/v) alginate with different Au^{3+} concentrations particularly 0.25, 0.5 and 1 mM. The UV-vis absorption spectra (Fig. 1) of Au-NPs solutions showed the maximum absorption wavelengths (λ_{max}) at 524, 529 and 531 nm for Au^{3+} concentrations of 0.25, 0.5 and 1 mM, respectively. The TEM images and the corresponding size distributions taken on those three colloidal Au-NPs were showed in Fig. 2. The average diameters for the Au-NPs were 5, 8 and 20 nm for Au^{3+} concentrations of 0.25, 0.5 and 1 mM, respectively. Results showed that as the Au^{3+} concentration increased the Au-NPs became bigger, which also indicated by the red shift of λ_{max} to longer wavelengths. The similar results were also observed earlier by Li et al. (2007) using poly (N-vinyl pyrrolidone) as stabilizer for preparation of Au-NPs.

2. Effect of alginate concentration

The dependence of Au-NPs size on the alginate concentration of 0.25, 0.5 and 1.0 % (w/v) while the Au^{3+} concentration fixed at 0.5 mM was studied. As the alginate concentration increased, the λ_{max} and the Au-NPs size of corresponding colloids decreased (Table 1). It can be seen from Table 1 that the critical concentration of alginate for obtaining smallest Au-NPs (~8 nm) was 0.5 % for 0.5 mM Au^{3+} by γ-irradiation with dose rate of approximately 1.3 kGy/h. Pal et al. (2005) also studied the effect of alginate concentration on the λ_{max} and size of Au-NPs prepared by UV photoactivation method. The obtained Au-NPs with λ_{max} at 527 nm (d~8.6 nm), 530 nm (d~12.4 nm) and 534 nm (d~14.4 nm) with respect to alginate of 0.1, 0.05 and 0.01 % were almost similar to our results but they used 0.25 mM Au^{3+} concentration.

Table 1. λ_{max}, optical density (OD) and diameter (d) of Au-NPs with different alginate concentrations

Sample	λ_{max}, nm	OD	d, nm
Au^{3+} 0.5 mM /Alginate 0.25 %	531.0	0.44	13 ± 1
Au^{3+} 0.5 mM /Alginate 0.5 %	529.5	0.48	8 ± 2
Au^{3+} 0.5 mM /Alginate 1 %	526.5	0.39	8 ± 1

3. Enlargement of seed particles

The Au-NPs with diameter of ~20 nm as prepared from solution of Au^{3+} 1 mM/0.5 % alginate were used as seeds for preparation of particles with larger diameter. In the enlargement step, a required amount of metal seed particles, metal salt and sodium alginate were mixed and irradiated for the growth of the seeds diameter. At this stage, the preformed seeds act as nucleation centers and become larger due to the reduction of the added metal ions on surface of the seeds. The average diameters of the obtained Au-NPs were of 21.1, 26.6, 39.1 and 37.8 nm for $[Au^{3+}]/[Au^0]$ = 2, 4, 6 and 8, respectively (Fig. 3). The TEM image in Fig. 3c revealed that at $[Au^{3+}]/[Au^0]$=6, the enlarged Au-NPs were more monodisperse and their average diameter was nearly double larger (40 nm) than that of the seeds (20 nm). This result was relatively compatible with the result of Henglein et al. (1999) when they synthesized Au-NPs by enlargement of seed particles at $[Au^{3+}]/[Au^0]$=7 using γ-irradiation. However, with the excessive presence of Au^{3+} at $[Au^{3+}]/[Au^0]$=8, the size of Au-NPs was not further increased but dispersed in two size ranges (Fig. 3d). Beside the main large Au-NPs with diameter of 37.8 nm, the small Au-NPs less than 10 nm were also formed. The reason may be due to the formation of new clusters from reduction of Au^{3+} to Au^0 in solution. This indicated that the enlargement of seed Au-NPs using alginate as stabilizer prepared by γ-irradiation with dose rate of approximately 1.3 kGy/h is applicable for $[Au^{3+}]/[Au^0]$ up to 6. Nevertheless, Sau et al. (2001) reported a non-iterative seed mediation which starting seeds were of ~20 nm and $[Au^{3+}]/[Au^0]$ varied from 2 to 100 with the diameters increased continuously from 30 to 110 nm. This result may be because they used UV-irradiation method for synthesis of seed and ascorbic acid reductant for particles growth process, which lead to the different enlargement of seed particles. Therefore, further studies should be carried out to clarify this phenomenon.

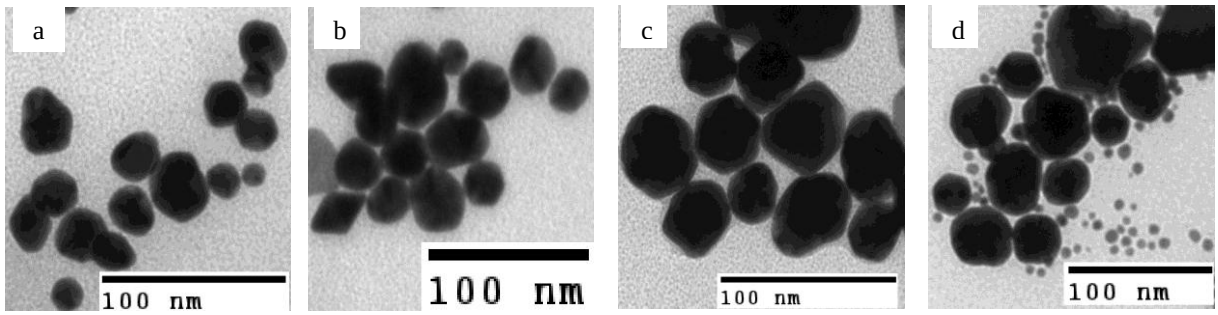

Figure 3. TEM images of Au-NPs obtained by enlargement of seed particles for $[Au^{3+}]/[Au^0]$=2 (a), 4 (b), 6 (c) and 8 (d).

IV. CONCLUSIONS

In conclusion, this work described an effective γ-irradiation method for preparation of Au-NPs using sodium alginate as stabilizer. The size of Au-NPs depended on the concentration of Au^{3+} and alginate. The double larger size (40 nm) and more monodisperse of Au-NPs were obtained by enlargement of seed particles (20 nm) at $[Au^{3+}]/[Au^0]$=6. The alginate stabilized Au-NPs with different sizes from 5 to 40 nm may be useful for biological applications owing to biocompatibility of sodium alginate.

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